Catalytic Investigation of Aluminum Effects on Benzene Hydrogenation Selectivity over Nickel Supported HMS/HZSM-5 Composites

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Ni/Al-HMS/HZSM-5 catalysts with varying amounts of Si/Al ratios were prepared *via* the impregnation method and evaluated for the hydrogenation of benzene at 130-190 °C. To study the catalyst characterization, various methods were used, such as X-ray diffraction, X-ray fluorescence, Fourier transform infrared spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, temperature-programmed desorption of ammonia, H_2 chemisorption, N_2 adsorption-desorption and thermogravimetric analysis. The effect of reaction temperature and residence time on catalytic performance was considered and kinetic of this reaction was investigated under different pressures. The results demonstrated that the composite catalysts have high benzene conversion (~80%), medium to low toluene and xylene conversion (16-80%), moderate benzene selectivity (~50%) in the mild reaction condition, and good catalytic stability against the coke deposition.

Keywords: Hydrogenation of benzene, Composite catalyst, Kinetic, Selectivity, Stability

INTRODUCTION

The presence of high amounts of aromatics in gasoline can reduce the quality of the fuel and also produce harmful gases [1,2]. Due to the problems that these gases cause for human health and the environment, governments have passed regulations to adjust the composition of materials in gas fuels and reduce the amount of aromatic compounds [3-5].

There are many methods for reducing the aromatics of gasoline such as removal from a precursor, alkylation, and solvent extraction. All of these methods have high costs, and hence, the reduction of aromatic compounds among these methods have attracted considerable attention of many researchers [6-8]. While many actions have been made during the last decades in the field of catalytic hydrogenation reactions, the hydrogenation of aromatic compounds still face many difficulties due to the stability

caused by aromaticity of these compounds. The formation of coke on the active sites of catalysts and the strict reaction conditions are other challenges to be dealt with.

Despite the introduction of homogeneous catalysts in this field [9], many of the catalysts used for the aromatic hydrogenation are supported metallic heterogeneous catalysts [10-13]. In recent years, many studies have demonstrated that bimetallic catalysts have higher activity, selectivity, and stability compared to single-metal species due to the positive synergistic effect of two metals. Bimetallic catalysts have been used for a variety of the hydrogenation reactions, including benzene hydrogenation [7,14-15].

Herein, Al-HMS/HZSM-5 supported Ni catalysts with various Si/Al ratios were prepared via the impregnation method and evaluated during the selective hydrogenation reaction of benzene in a mixed solution. The HMS/HZSM-5 support has dual micro- (HZSM-5) and meso- (HSM) pores that combine the properties of both these supports, including the acidity of HZSM-5 and the high surface of the HSM

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[16]. To increase the acidity desired for the hydrogenation reaction, the aluminum has been used in the catalyst texture [17]. Nickel metal has also been selected as the active phase, due to its excellent effects on this reaction and cost-effectiveness [10]. The main goal of this work is to find and optimize the best Si/Al ratio in our supported metal catalysts according to the high amounts of conversion, selectivity and stability resulted from the catalytic performances. The physicochemical properties of the prepared catalysts were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR), ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS), Brunauer-Emmett-Teller (BET) equation, thermo-gravimetric and differential thermal analyses (TG/DTA), and temperature-programmed desorption of NH_3 (NH_3-TPD) techniques. In this work, the reaction kinetics and the effects of reaction temperature and residence time on the catalytic activity and stability were also studied.

EXPERIMENTAL

Catalyst Preparation

The Al-HMS/HZSM-5 alumina-silicate support with various molar ratios of Si/Al were prepared according to the method reported by our group [16,17]. In this preparation method, 1 g of HZSM-5 (Zeolyst International; Si/Al = 14) was added to appropriate amounts of ethanol, tetraethyl orthosilicate, dodecyl amine, hydrochloric acid (1 M), aluminum isopropoxide solution, and distilled water. The product was filtered and dried overnight at 110 °C and calcined in the air with a heating rate of 1 °C min^{-1} to 600 °C for 6 h.

Ni supported catalysts were prepared by the impregnation method with appropriate amounts of nickel(II) nitrate hexahydrate solution. After evaporation of the solvent, these catalysts were dried overnight in air at 110 °C and calcined at 300 °C for 4 h. The resulting Ni/Al(x)-HMS/HZSM-5 catalysts were labeled Ni/Al(x)-HZ, where x represents the nominal Si/Al ratios (that are equal to 20, 35 and 45).

Catalyst Characterization

Silicium to aluminum ratios and metal contents were measured by XRF-8410 Rh apparatus and a voltage of 60 kV. Powder XRD patterns were recorded on an X-PERT diffractometer using Ni-filtered Cu k$_\alpha$ radiation at 45 kV and 50 mA with a 0.06° 2θ-step and 1 s per step.

FTIR spectroscopy was used for identification of chemical bonds in the prepared hybrid catalysts. The analysis was performed on a BOMEM FTIR spectrophotometer model Arid-Zone MB series in a wavenumber range of 400-4000 cm^{-1} with appropriate amounts of the catalysts and KBr for preparing the tablets.

UV-Visible DRS was recorded on a Shimadzu UV-2100 UV-Vis spectrophotometer using $BaSO_4$ as a reference. The powder catalysts were evaluated in 200-800 nm at room temperature.

To determine nitrogen adsorption isotherms, the calcined catalysts were outgassed for 3 h at 573 K, and then, they were recorded at 77 K on an ASAP-2010 micromeritics (USA) apparatus. BET equation was used to evaluate the volume of the adsorbed monolayer (V_p). The specific surface area (S_{BET}) was calculated by assuming an N_2 molecule to cover 0.162 nm^2. The Barret-Joyner-Halenda method to the adsorption branches of the N_2 isotherms was applied for calculating the average pore diameter (d_p).

To investigate the amounts of acidic sites, NH_3-TPD was carried out with a TPD/TPR analyzer (2900 Micromeritics) instrument. A total of 0.2 g of each sample was pretreated at a heating rate of 10 °C min^{-1} to 600 °C for 1 h under helium flow (40 ml min^{-1}). After cooling to 100 °C, 10 Vol% of NH_3-He flow was introduced until the acid sites of the catalysts were saturated with NH_3. Afterward, the desorption profiles were recorded from 25 to 800 °C with a heating rate of 10°C min^{-1}.

For evaluation of the dispersion of the metals, H_2 pulse chemisorption experiments were conducted on a TPD/TPR analyzer (2900 Micromeritics) equipped with a thermal conductivity detector (TCD). Briefly, 0.2 g of each catalyst was subjected to reduction for 1 h at 450 °C, followed by purging in an argon flow at 500 °C for 1 h. After cooling to room temperature, pure hydrogen (14 ml min^{-1}) was injected in pulses until no further adsorbed hydrogen on the catalysts.

Thermogravimetric and differential thermal analysis (TG/DTA) were performed on an STA503 M instrument for evaluating the coke depositions and stability of the prepared catalysts. A total of 20 mg of the samples was measured

under an air atmosphere with 5 Vol% O_2/N_2 gas mixture (60 ml min^{-1}) and heated from 25 to 800 °C at 10 °C min^{-1}.

Catalytic Reaction Tests and Methods of Calculation

Activity. 1 g of each catalyst was loaded into a continuous fixed-bed Pyrex reactor, operated under isothermal conditions and connected to an online gas chromatograph (Agilent Technologies 7890A equipped with a flame ionization detector) by means of a controller. The test was carried out at atmospheric pressure, a reaction temperature ranging from 130-190 °C with a heating rate of 20 °C h^{-1}, a liquid feed flow rate (pure or mixed of benzene, toluene, and xylene) equal to 2 ml h^{-1}, and a hydrogen flow rate equal to 40 ml min^{-1}. Before starting the run, the catalyst was kept in a hydrogen stream under 450 °C for 2 h to pre-reduce the metallic function. Catalytic activity is expressed in terms of conversion, which is defined as a fraction of each aromatic compound, which have reacted. Also, overall aromatic conversion (O_C) for a mixed solution of 6 Vol% of benzene (B), 8 Vol% of toluene (T), and 8 Vol% of xylene (X) in n-heptane was calculated by the following equation:

$$O_C \text{ (\%)} = (m_B C_B + m_T C_T + m_X C_X) \times 100 \qquad (1)$$

where m and C are the molar ratio and conversion in benzene/toluene/xylene mixture, respectively. The following equation was used for calculating the selectivity (S):

$$S_B \text{ (\%)} = \frac{m_B C_B}{O_C} \times 100 \qquad (2)$$

Stability. The major problem in the catalytic processes is the coke deposition on the surface of the catalysts and their deactivation. Therefore, the stability of the prepared catalysts for further study about the influence of acidity and also, Si/Al amounts in the catalytic performance were examined under the operating conditions similar to the activity tests at a selected constant temperature (150 °C according to the best selectivity to benzene) for 10 h on stream. The products were also identified with an online gas chromatograph.

Kinetic study. A kinetic study was carried out to determine the reaction order and activation energy for hydrogenation of benzene over Ni/Al(x)-HZ. The reaction orders with respect to the benzene concentration (2-8 Vol%) and hydrogen pressure (2.6-5.9 Pa) were estimated at various temperatures ranging from 130-190 °C. In this method, the partial pressures of hydrogen and benzene were changed, respectively, for evaluating the order of benzene and hydrogen. In all experiments, the reaction mixtures were analyzed using gas chromatography at a fixed interval of time.

RESULTS AND DISCUSSION

Catalyst Characterization

After calcination, the Si/Al ratios and the metal contents for Ni/Al(x)-HZ catalysts were determined by the XRF method. The results were in close agreement with the expected theoretical amounts (Table 1).

The powder XRD patterns of calcined Ni/Al(x)-HZ with various amounts of Si/Al ratios (20, 35 and 45 wt%) are shown in Fig. 1. These patterns for the catalysts exhibit intense peaks at low angles (2.3°), which is a characteristic of the HMS framework. The peaks at 6-11° and 22-25° are due to ZSM-5 phases, and a broad diffraction line between 20° and 30° observed in the spectra demonstrates the amorphous part of HMS. It can also be seen that the intensity of the HMS peak increases and its width decreases with reducing the Al amount, indicating that the incorporation of aluminum is associated with an increase in lattice disorder. Ni phase (NiO) XRD peaks occur at 2θ = 37.4°, 43.3°, 64.3°, 75.5° and 79.4°.

The FTIR spectra were also recorded at room temperature (Fig. 2). These spectra show the bands of physisorbed water at around 1600 and 3400 cm^{-1}. The characterization bands of HMS are seen at 1200, 1100 and 440 cm^{-1}, which are assigned to the asymmetric stretching and bending modes of ≡Si-O-Si≡. The characterization bands of ZSM-5 part of these composite catalysts appeared at around 1000, 790 and 540 cm^{-1} which are due to the asymmetric and symmetric stretching vibration bands of framework Si-O-Si bands and the vibration double ring in the microporous HZSM-5, respectively.

Table 1. Physicochemical Properties of the Prepared Catalysts

Catalyst	Ni/Al(20)-HZ	Ni/Al(35)-HZ	Ni/Al(45)-HZ
S_{BET} (m^2 g^{-1})	629	679	735
V_p (cm^3 g^{-1})	0.87	0.90	1.04
S_{micro} (m^2 g^{-1})	115	125	135
$V_{micro-p}$ (cm^3 g^{-1})	0.31	0.32	0.37
d_p (nm)	5.53	5.30	5.66
Weak acid[a]	0.69	0.38	0.19
Strong acid[a]	0.84	0.59	0.36
Si/Al[b]	18.21	33.92	44.16
Ni (%)[b]	24.32	24.39	24.51
M_d (%)[c]	27.3	29.7	23.3

[a]Weak and strong acids (mmol$_{NH3}$ g^{-1}). [b]By XRF method. [c]Metal dispersion from H_2 chemisorption.
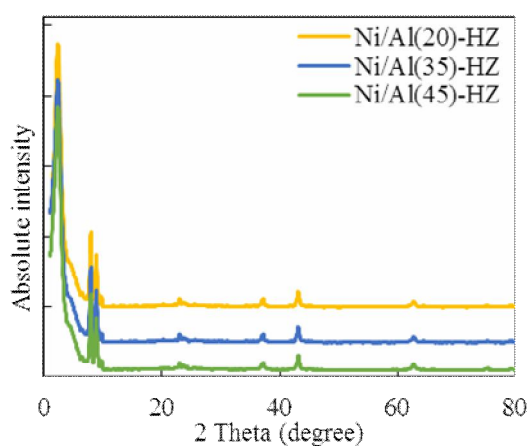
Fig. 1. The XRD patterns of the prepared catalysts.

Textural properties of the prepared materials were determined by nitrogen physisorption that its results are listed in Table 1. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the Ni/Al(x)-HZ catalysts follow isotherm type IV with H1 hysteresis loops which are characteristics of mesoporous materials with highly uniform cylindrical pores. These isotherms have two steps of capillary condensation. The first step at $P/P_0 = 0.3$ due to intraparticle mesoporosity inside these catalysts, and the second step at $P/P_0 = 0.9$ with a small hysteresis loop attributed to interparticle textural porosity, indirectly representing the size of particles; smaller particle size demands higher partial pressure. The results of the BET surface area for the synthesized material
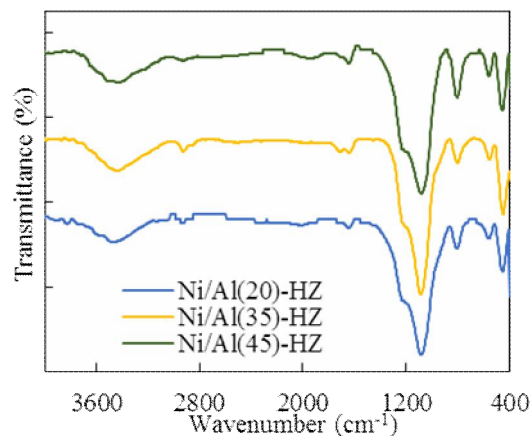
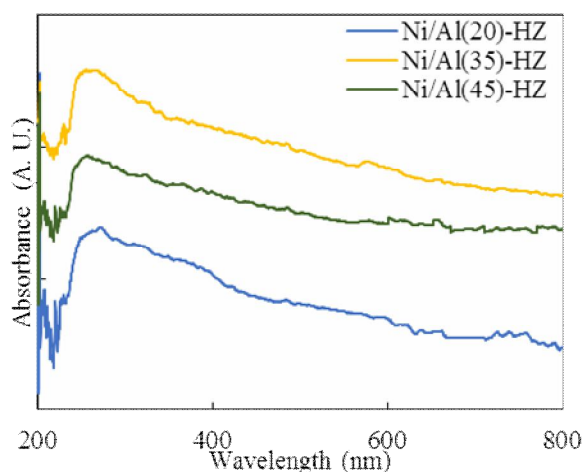**Fig. 2.** The FTIR spectra of the Ni/Al(x)-HZ catalysts.

Fig. 3. The UV-Vis DRS for named catalysts.

change as follows:

Ni/Al(45)-HZ > Ni/Al(35)-HZ > Ni/Al(20)-HZ

Table 1 demonstrates also the textural characterization (S_{BET}, V_p and d_p) results for the catalysts. It can be concluded from the results that increasing the Si/Al ratio results in an enhancement for textural characteristics of the prepared catalysts. By increasing Al amounts, a decrease in the pore volume and surface area is observed and there is no significant change in pore diameter.

The acidity distributions on the surface of the catalysts are also listed in Table 1. The amounts of weak acid for these catalysts are in the range of 0.19-0.68 mmol g_{cat}^{-1}, and those of strong acid are in the range of 0.36-0.83 mmol g_{cat}^{-1}. These catalysts have two desorption peaks in the temperature region of 100-600 °C, interpreted as the desorption peaks of the weak and strong acids. The summarized results are evolving by the following trends:

Ni/Al(45)-HZ > Ni/Al(35)-HZ > Ni/Al(20)-HZ

Catalytic Performance in Selective Hydrogenation of Benzene

The catalytic performance of the composite catalysts was tested and investigated with a series of aromatic

compounds as a model reaction for the hydrogenation reaction of gasoline. This includes benzene, toluene, and xylene (pure and mixed solution). Cyclohexane, methyl cyclohexane and dimethyl cyclohexane were the only products in these hydrogenation reactions, indicating total hydrogenation of materials over the catalysts.

Figure 4 shows the benzene, toluene and xylene conversions at pure solutions and also overall conversion and benzene selectivity at a mixed solution in 1 h on stream over the prepared catalysts. As it can be seen in this figure, the increase of temperature resulted in increased benzene hydrogenation and decreased toluene hydrogenation. Ni/Al(45)-HZ catalyst shows the best conversion for benzene and xylene at all temperatures, but Ni/Al(20)-HZ has the highest toluene conversion. The benzene conversion is the highest value for all catalysts at 190 °C. Among the studied catalysts, the Ni/Al(20)-HZ catalyst has the lowest benzene conversion and is equal to 60% at 130 °C. This catalyst for toluene hydrogenation shows the highest conversion (over 50%), whereas Ni/Al(45)-HZ has the lowest toluene conversion in all temperatures. Xylene conversion does not follow a linear trend and has the highest amounts in 130 °C. From 150 to 190 °C, an increase is observed in xylene conversion. In terms of overall conversion, Ni/Al(35)-HZ catalyst at 130 °C and Ni/Al(45)-HZ catalyst at other temperatures achieved high conversion.

Regarding the benzene selectivity of the catalysts in the ternary solution, Ni/Al(35)-HZ catalyst shows the best benzene selectivity at all temperatures. It can be inferred from these results that the best temperature for the selective performance is 150 °C.

Briefly, Ni/Al(35)-HZ catalyst had a benzene conversion of 68% that is better benzene selectivity compared to other catalysts at 150 °C. This indicates that Ni/Al(35)-HZ catalyst has a high activity and selectivity for benzene hydrogenation at low temperatures.

The stability of the prepared catalysts was measured during 10 h on stream at 150 °C (Fig. 5). It was observed in all catalysts that the catalytic activity decreases with time until it is constant. The toluene conversion was almost constant, but the benzene and overall conversions decrease slightly during the period of time. The xylene conversion diminishes significantly in the first hours which increases

the benzene conversion. The lowest and highest decreases in the conversion were observed for Ni/Al(20)-HZ and Ni/Al(45)-HZ, respectively. The best benzene selectivity (above 60%) after 10 h was observed for Ni/Al(35)-HZ, indicating a good stability of this catalyst than others.

The loss of activity can be due to the rapid formation of coke at the early hours after the reaction. For this reason, the deposition of coke on the catalyst surface was measured using TGA. The results show that the maximum (7.9 wt%) and minimum (5.4 wt%) amounts of coke were deposited on Ni/Al(20)-HZ and Ni/Al(35)-HZ catalysts, respectively.

Kinetic Study for Benzene Hydrogenation

The kinetic study was done over the prepared catalysts in low conversion conditions (<10%). Because in this situation, a linear Arrhenius plot has low error. The apparent activation energies (E_{app}^{act}) were measured by the logarithmic form of the Arrhenius equation under conditions mentioned in the experimental section,

$$\ln k = \ln A - \frac{E_{app}^{act}}{RT} \tag{1}$$

where k is the rate constant of reaction and A is a pre exponential factor. It should be noted that, in this study, the reaction rate is defined as follows;

$$r \, (mol \, g^{1} \, s^{-1}) = \frac{Benzene \, flow \, rate \, (ml \, s^{-1}) \, . \, Benzene \, density \, (g \, ml^{-1}) \, . \, Conversion \, (\%)}{Benzene \, molar \, weight \, (g \, mol^{-1}) \, . \, Weight \, of \, catalyst \, (g) \, . \, Im \, pregnated \, metal \, (wt\%)} \tag{2}$$

The reaction orders were measured by the following empirical kinetic equation:

$$r \, (mol \, g^{-1} \, s^{-1}) = k P_{H_2}^{n} \, P_{B}^{m} \tag{3}$$

where n and m are the partial orders of hydrogen and benzene, respectively.

To measure the reaction order of benzene (m_B), the catalysts were examined in a temperature range of 130-190 °C for a series of reaction mixtures containing various concentrations of benzene (2-8 Vol% with 2 ml min^{-1} flow rate) while the H_2 flow rate was kept constant at 40 ml min^{-1}. After each test, the catalysts were
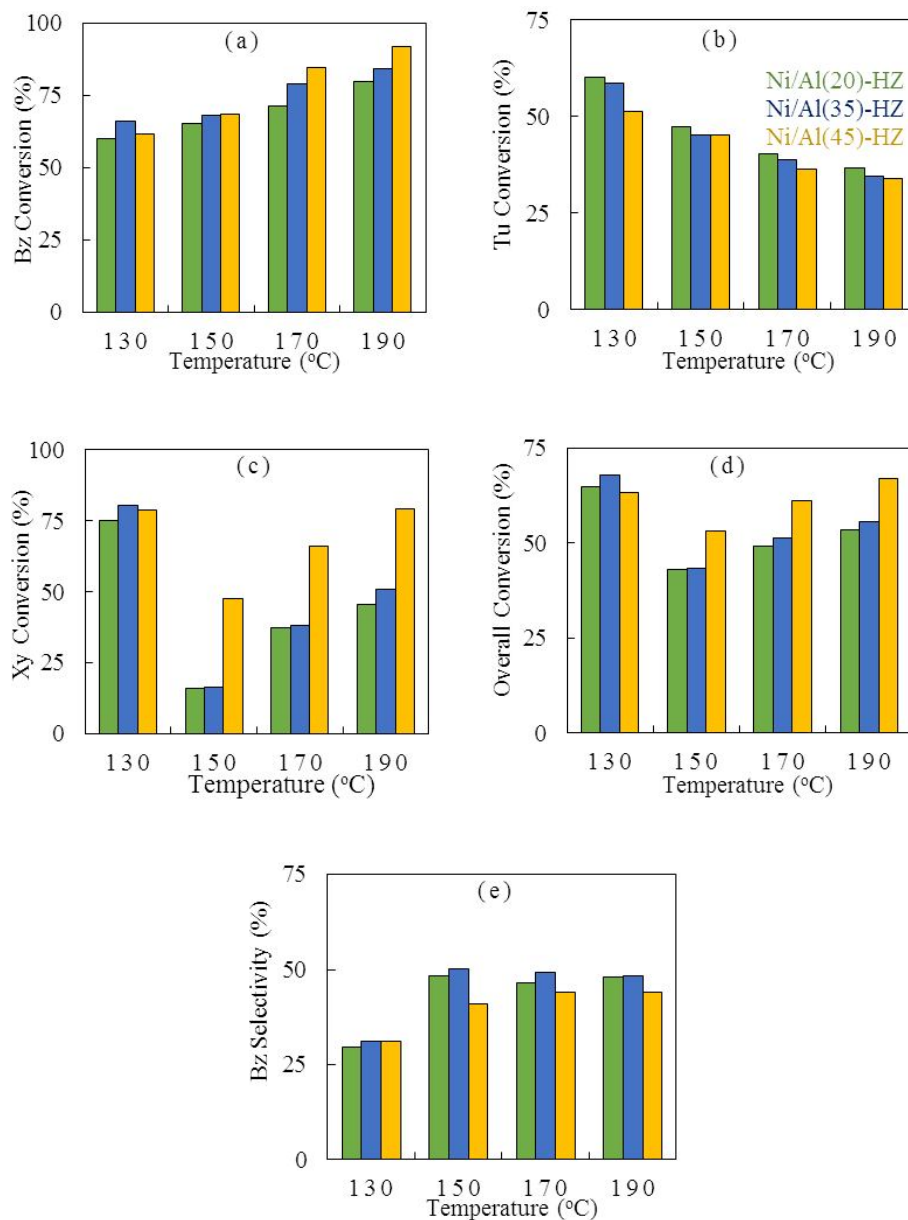
Fig. 4. The temperature effect on (a) Bz conversion, (b) Tu conversion, (c) Xy conversion, (d) overall conversion and (e) Bz selectivity.

cleaned with a flow of H_2 at 350 °C before cooling to 130 °C and continuing the other steps of the reaction. The reaction order of H_2 (n_{H2}) was obtained in the same method. In this step, the flow rate of H_2 was changed between 20 and 45 ml min^{-1} while maintaining the benzene at 6 Vol% with 2 ml min^{-1} flow rate. Figure 6 shows the dependence of the reaction rate on the partial pressure of hydrogen and benzene.

A summary of activation energies and the reaction orders of benzene and hydrogen are reported in Table 2. The reaction rate increases with hydrogen partial pressure, whereas it decreases or remains almost constant with the benzene partial pressure.

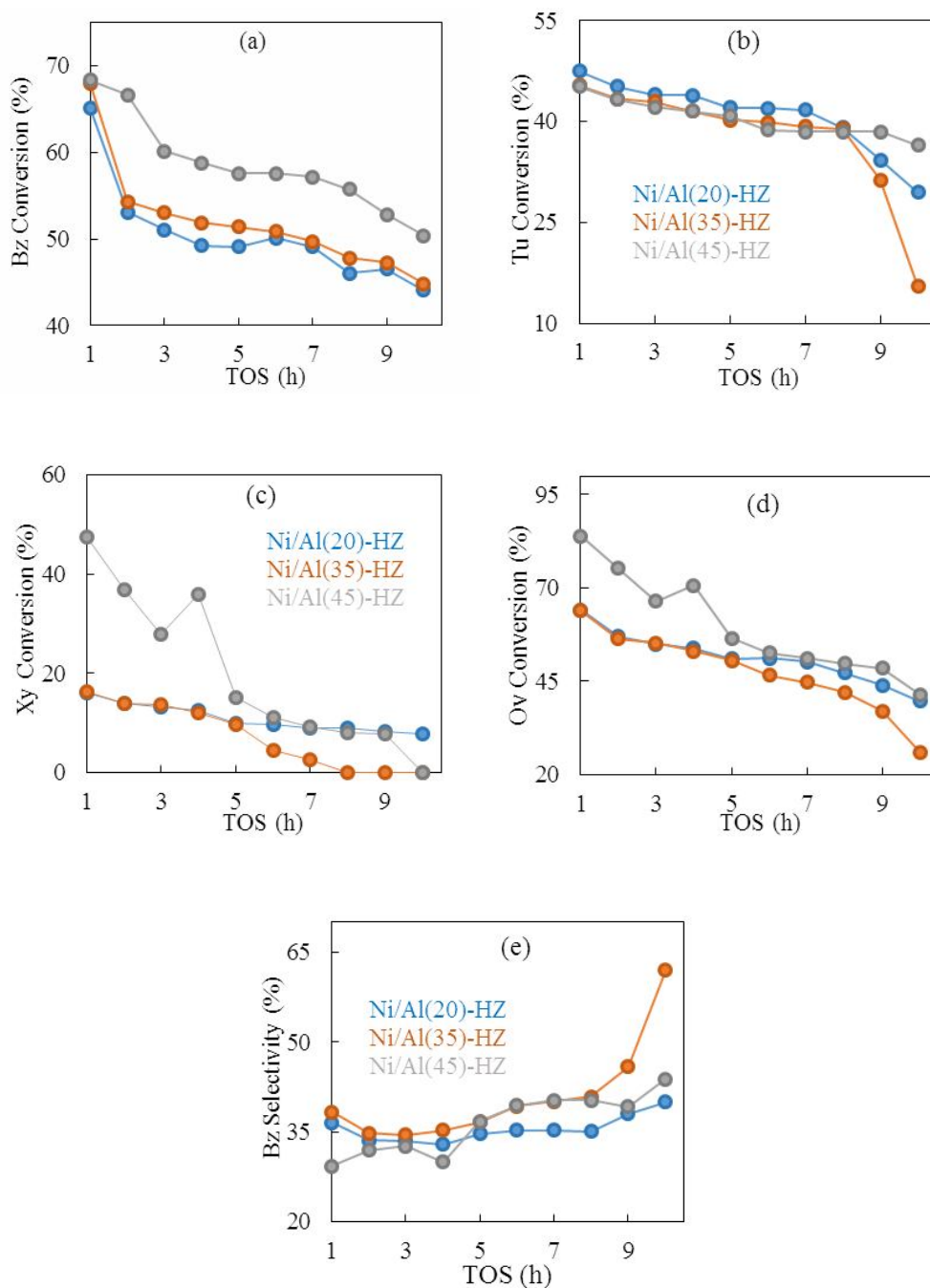The reaction orders were measured 0.00, -0.32 to -0.26

Fig. 5. The effect of time on stream (10 h) over (a) Bz conversion, (b) Tu conversion, (c) Xy conversion, (d) overall conversion and (e) Bz selectivity for Ni/Al(x)-HZ catalysts at 150 °C for the hydrogenation reaction.

and -0.22 to -0.16 for benzene on composite catalysts of Ni/Al(x)-HZ (x = 20, 35 and 45) at a constant temperature, respectively, whereas for hydrogen, the reaction orders were

found to be 0.76-0.82, 0.62-0.69 and 0.71-0.80, respectively (Table 2). These results are relatively similar to the literature data [18]. The negative order for benzene indicates
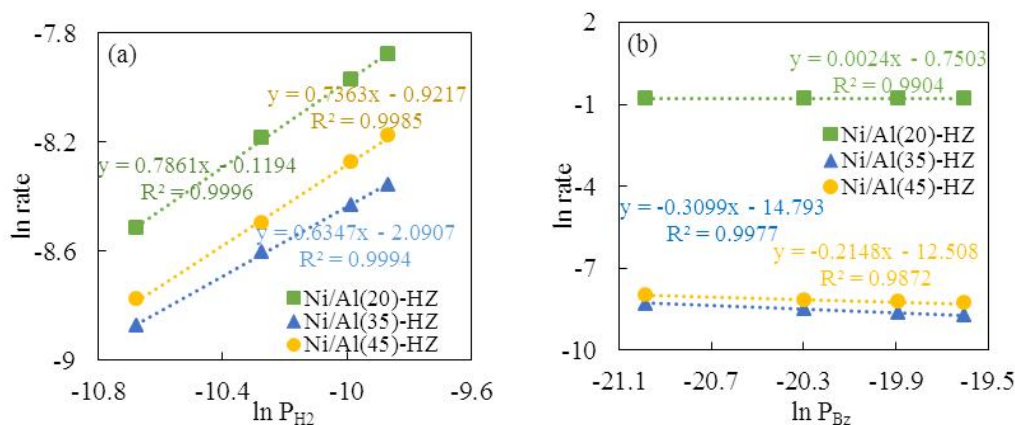
Fig. 6. Double-log plots of the Bz hydrogenation reaction rate *versus* the partial pressures of (a) hydrogen and (b) Bz at a selected temperature (150 °C) for the prepared catalysts.

Table 2. Kinetic Parameters for the Benzene Hydrogenation

Catalyst	Ni/Al(20)-HZ		Ni/Al(35)-HZ		Ni/Al(45)-HZ	
order	n_{H2}	m_B	n_{H2}	m_B	n_{H2}	m_B
T = 130 °C	0.76	0.00	0.62	-0.32	0.71	-0.22
T = 150 °C	0.79	0.00	0.63	-0.31	0.74	-0.21
T = 170 °C	0.81	0.00	0.67	-0.27	0.78	-0.17
T = 190 °C	0.82	0.00	0.69	-0.26	0.80	-0.16
E_{app}^{act} (kJ mol^{-1})	39.71		23.60		21.78	

its self-inhibition on bimetallic catalysts. As can be seen in this table, the reaction orders of H$_2$ and benzene increase with reaction temperature, probably due to a substantial decrease in the coverage of each reactant.

The results of apparent activation energies (Table 2) were also in good agreement with the ones reported in the literature for nickel loaded on various supports [19]. The activation energies for the reaction of benzene hydrogenation calculated from the Arrhenius plot are 39.71, 23.60 and 21.78 kJ mol^{-1} for the prepared catalysts, respectively. The kinetic study of the activation energy indicates that the benzene hydrogenation carried out on Ni/Al(45)-HZ (21.78 kJ mol^{-1}) is easier and faster than that of other prepared catalysts.

CONCLUSIONS

In summary, a series of micro/mesoporous catalysts with different amounts of Si/Al ratios was successfully prepared by the impregnation method. Catalytic characteristics were studied using different analysis methods. It can be concluded from the conversion, selectivity, and stability results that the best catalytic behavior was reached with Ni/Al(35)-HZ catalyst at 150°C, with good benzene conversion (68%), the highest benzene selectivity (50%), and lowest coke formation (5.4 wt%). The results prove the important impact of active phase dispersion (M$_d$) and the catalytic acidity in the hydrogenation reaction of benzene. Additionally, kinetic

tests performed under various conditions showed that this catalyst could perform the hydrogenation reaction with an appropriate rate. The activation energies calculated in this work confirm that bimetallic catalysts supported on micro/mesoporous molecular sieves are attractive supports for the selective hydrogenation of benzene.

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